

4-9211

GASIFICATION REACTIVITIES OF ULTRASONICALLY  
TREATED COALS

Prepared for:

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Final Report  
Contract No. OST84-00352  
November 1, 1984 - April 30, 1985

May 31, 1985

55 pp.

EST 11 85  
MICROMEDIA

#### ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Dr. B.N. Nandi, Dr. E. Furimsky and the technical staff in the analytical section of E.R.L. at CANMET. We would like to thank Mr. G.K. Diedrich for his help in securing some of the equipment needed for this work.

### ABSTRACT

Ultrasonic irradiation was applied to the processing of Balmer coal rejects and Prince coal. Balmer rejects were treated in: dilute hydrochloric acid, water and solutions of ammonia in methanol. Prince coal was treated in water and solutions of ammonia in methanol only. The rate of demineralization of the Balmer rejects by dilute hydrochloric acid was slightly increased when intense ultrasound was applied. Treatment of Balmer rejects and Prince coal in water resulted in significant comminution. The surface area of the Balmer rejects (on a dry, ash free basis) was not affected by treatment with ultrasound in water. Treating Balmer rejects with ammonia/methanol solutions had no significant effect on their ash content, regardless of whether or not ultrasound was applied. The ash and sulfur content was not significantly affected by any of the treatments.

## EXECUTIVE SUMMARY

The nature of western Canadian coals makes them very difficult to clean. The rejects remaining after cleaning western coals (such as Balmer coal) still contain as much as 50% organic material. This material is a potentially valuable resource if it can be economically upgraded. Similar difficulties are encountered in removing sulfur from some high sulfur eastern Canadian coals (such as Prince coal). Obstacles such as these prevent the complete utilization of Canadian coal resources.

The application of intense ultrasound to coal beneficiation has been the subject of several recent investigations. Improvements in economy, performance and efficiency have been reported for physical methods such as flotation and oil agglomeration in some of this work. Other reports cite reductions in the severity of conditions and duration of treatment required to effect significant sulfur reductions by several chemical techniques. This results in a reduction of the net energy cost required to process the coal. Other processes such as solvent extraction, leaching of non-coal minerals and oxidations have been substantially accelerated and improved with the application of intense ultrasound.

In view of the above, an exploratory study of the use of ultrasound in processing a western Canadian coal reject (Balmer) and a high sulfur eastern Canadian coal (Prince) was undertaken in order to assess the potential for improving their utilization. The effect of treating Balmer rejects and Prince coal with ultrasound in several liquids was studied in this work.

Balmer rejects were treated in: dilute hydrochloric acid, water and solutions of ammonia in methanol. Prince coal was treated in water and ammonia/methanol solutions only. The rate of Balmer reject demineralization by dilute hydrochloric acid increased slightly (up to 1.6%) when intense ultrasound was applied. Treatment of both Prince coal and Balmer rejects in water caused significant comminution. After 120 min of treatment with ultrasound in water, 33% of Balmer rejects (which were originally 35 x 60 mesh) were able to pass through a 60 mesh screen. No change in the surface area of Balmer rejects (on a dry, ash free basis) was observed after treatment. The ash content of Balmer rejects was not significantly affected by treatment in ammonia/methanol solutions.

No significant change in either ash or sulfur content of

the Prince coal occurred after any of the treatments employed in this work. Prince coal was visibly darker and shinier after treatment with ammonia/methanol. This likely indicates some chemical change in the coal surface as a result of treatment.

The amount of coal supplied by CANMET during the course of this work was not sufficient to carry out a study of the effects of treatment on gasification reactivities of ultrasonically treated coals. Such a study would provide a better assessment of the efficacy of any given treatment.

## RÉSUMÉ

La nature même du charbon de l'ouest canadien le rend difficile à nettoyer. Avec le traitement actuel, ce charbon (par exemple, celui des mines de Balmer) donne un résidu qui contient encore jusqu'à 50% de matières organiques. Ce résidu gagnerait une valeur commerciale s'il pouvait être bonifié économiquement. On rencontre des difficultés du même ordre lorsque l'on veut séparer le soufre du charbon de l'est canadien (mines de Prince) à cause de sa haute teneur en soufre. Des problèmes de ce genre empêchent l'utilisation plus complète des ressources du charbon canadien.

Plusieurs études ont déjà fait état des progrès accomplis par l'utilisation d'ultrasons intenses. Des méthodes physiques, telles la flottaison et l'aggrégation à l'huile, se sont trouvées améliorées en terme d'économie, de performance et d'efficacité. D'autres rapports indiquent que la séparation du soufre peut être effectuée avec des conditions expérimentales plus douces tout en réduisant la durée du traitement lorsque des ultrasons sont combinés à des méthodes chimiques. Cela amènerait une diminution du coût net en énergie pour le traitement du charbon. D'autres procédés, tels l'extraction par solvants, le "leaching" de minéraux non-carbonifères et l'oxygénation, ont été accélérés et rendus

plus efficace à l'aide d'ultrasons intenses.

Le but de ce projet est d'explorer l'utilisation des ultrasons pour améliorer le recyclage des résidus de charbon de l'ouest canadien (mines de Balmer) et la séparation du soufre du charbon de l'est canadien (mines de Prince). Ce rapport présente les effets des ultrasons sur les résidus de Balmer et le charbon de Prince dans différentes solutions.

Les résidus miniers de Balmer ont été traités avec: (i) de l'acide chlorhydrique dilué, (ii) de l'eau distillée et (iii) des solutions d'ammoniac dans du méthanol. Alors que le charbon des mines de Prince a été traité avec de l'eau distillée et des solutions d'ammoniac/méthanol seulement. Le taux de dissolution des minéraux (contenu dans les cendres) par l'acide chlorhydrique augmente légèrement (jusqu'à 1.6%) avec l'application d'ultrasons. Nos travaux montrent que l'utilisation des ultrasons dans l'eau distillée entraîne la fragmentation des échantillons. Après 120 minutes de ce traitement, le tiers des résidus (initialement 35 x 60 "mesh") parvenait à passer au travers d'un tamis de 60 "mesh". Il n'y a pas eu de changement notable dans la surface totale des résidus suite aux traitements. Pas plus que la quantité de cendres n'a été affectée par le traitement avec les solutions

ammoniac/méthanol ou l'eau distillée (mines de Balmer).

Aucun changement n'a été remarqué pour le contenu en cendres ou en soufre du charbon de Prince après les deux types de traitements mentionnés dans ce rapport. Le charbon était toutefois plus foncé et plus luisant après l'avoir passé à la solution ammoniac/méthanol. Cela laisse croire que la surface du charbon a subi des modifications chimiques.

La quantité d'échantillon de charbon fournis par CANMET pour ce projet n'était pas suffisante pour procéder à l'étude des effets du traitement aux ultrasons sur la reactivité de gaséification du charbon. Une telle étude permettrait une meilleure évaluation de l'efficacité des traitements.

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## INTRODUCTION

### (1) Objective

The objective of this work was to explore the potential use of intense ultrasound in the deashing of coal and coal rejects. Any improvements in this process could lead to the improved utilization of these materials for gasification and other purposes.

### (2) Rationale

Eastern Canadian coals have good washability characteristics, but some contain high levels of sulfur which is not as easily removed as the ash. Western Canadian coals do not have good washability characteristics (1). Such problems are impediments to the complete utilization of Canadian coal resources.

The rejects left after washing a western coal (eg. Balmer coal) still contain as much as 40 to 50% organic material. This material represents a potentially valuable resource if it can be upgraded for further use. However, these rejects have ash levels as high as 60% with much of this ash existing as finely disseminated clay materials (1). This clay material fills even the smallest fissures and pores within the coal structure. Consequently, beneficiation of this material is a

much more difficult task than beneficiation of the original coal.

The application of intense ultrasound to coal beneficiation has been the subject of several recent investigations (2-12). Improvements in economy, performance and efficiency have been reported for physical methods such as flotation (2-4,7-11) and oil agglomeration (5-7) in some of this work. Other reports cite reductions in the severity of conditions and duration of treatment (12) required to effect significant sulfur reductions by several chemical techniques. This results in a reduction of the net energy cost required to process the coal. Other processes such as solvent extraction (13,14), leaching of non-coal minerals (15,16) and oxidations (17) have been substantially accelerated and improved with the application of intense ultrasound.

Many of the effects associated with intense ultrasound in liquids may be attributed to acoustic streaming and/or acoustic cavitation. Acoustic streaming is a complex phenomenon which results in both microscopic and macroscopic flow of a liquid in a sound field. (A thorough explanation of this effect can be found in reference (18)). This may facilitate mixing on a microscopic scale, thereby accelerating

reactions in which the rate determining step is diffusion of reactants across some phase boundary.

Acoustic cavitation is a process whereby small transient cavities are formed in a liquid when the low pressure phase of an ultrasonic wave exceeds the tensile strength of the liquid. These cavities are rapidly compressed during the subsequent high pressure phase of the wave. The collapse is extremely rapid (of the order of  $10^{-6}$  s) and generates conditions of high temperature (of the order of  $10^3$  °C) and pressure (of the order of  $10^2$  atm) within the cavity (19). Very intense shock waves (up to  $10^2$  atm) are also generated within the liquid upon collapse of the cavities (19). These effects cause violent agitation within the liquid, erosion of surfaces (20), chemical reactions (21), scission of polymer chains (22) and homogenization of immiscible liquids.

Although the experiments conducted in this work were carried out using small-scale laboratory batches, the technology is available today to scale this up to large scale continuous operation. Commercial applications such as cleaning, welding of metals and plastics, and others have successfully used high powered ultrasonic equipment designed specifically for these purposes (23).

In view of the above, an exploratory study of ultrasonic processing of a western coal reject (Balmer) and a high sulfur eastern coal (Prince) was carried out to assess the possibility of improving their utilization.

## EXPERIMENTAL

### (1) Materials

#### (i) Coal Samples

Two samples (approximately 500 g each) of B.C. Balmer coal rejects were obtained from CANMET in Ottawa. The first sample had been sieved to 8 x 18 mesh, while the second sample appeared to contain particles no larger than 1 cm. Two samples (about 300 g each) of Nova Scotia Prince coal were also obtained from CANMET. One sample had been crushed to 20 x 0 mesh while the other had been crushed to 100 x 0 mesh. These amounts were insufficient to permit processing, analysis and gasification reactivity analysis of samples.

#### (ii) Reagents

Distilled water, anhydrous ammonia (Matheson), research purity carbon dioxide (Matheson), reagent grade: hydrochloric acid (Anachemia), carbon tetrachloride (Anachemia), bromoform

(Aldrich), tetrachloroethylene (Caledon), methanol (Caledon), 1,1,1-trichloroethane (Caledon) and varsol were used without further purification.

#### (iii) Ultrasonic Apparatus

Ultrasound with a frequency of 20 kHz was produced with a Bransonic W-350 Sonifier ultrasonic generator (Branson Sonic Power Company Division of Branson Ultrasonics Corporation, Danbury, Connecticut 06810) equipped with a standard titanium horn. A fixed acoustic intensity of  $21 \text{ W cm}^{-2}$  (determined calorimetrically) (24) was used.

#### (iv) Insonation Cell

Ultrasonic irradiation of the coal to be treated was carried out with the tip of the horn immersed directly in a coal slurry. Two glass insonation cells were used in this work. Initially, a large insonation cell with a volume of about 500 ml was used (see reference 25). This was abandoned in favor of a smaller spherical cell which had a volume of about 270 ml (see reference 24). This smaller cell provided much better mixing of the coal and more effective exposure of the coal to the ultrasound. The horn could be inserted into the cells through a large central opening located in both of the cells used.

## (2) Methods

### (i) Coal Sample Preparation

All samples were ground by hand using a mortar and pestle. The first sample of Balmer rejects was ground and separated into the following three size fractions: 0 x 18, 18 x 80, and 80 x 0 mesh. After consultation with Dr. Nandi at CANMET, it was decided to separate the second sample of Balmer rejects into the following size fractions: 18 x 35, 35 x 80, 80 x 120, and 120 x 0 mesh after grinding. The Prince coal samples were used without further preparation. All samples were stored in tightly closed glass jars prior to use.

### (ii) Ultrasonic Treatment

A preweighed sample of the coal to be processed was added to a known volume of suspending liquid. The cell was then attached to the ultrasonic horn and surrounded with an appropriate thermostat bath. The irradiation was initiated by turning on the ultrasound.

The temperature was measured using a single junction chromel-alumel thermocouple immersed in the slurry by way of a thermocouple well. The temperature of the slurry rose by

about 10 °C during the first 5 min of irradiation but remained constant to within  $\pm 1$  °C thereafter. After the insonation period, the sample was collected by suction filtration on a number 42 Whatman filter paper.

### (iii) Dense Medium Separation

Mixtures of tetrachloroethylene and bromoform or carbon tetrachloride and bromoform were prepared so that they had specific gravities of 1.65. Mixtures with specific gravities of 1.30 and 1.55 were prepared from tetrachloroethylene and varsol.

A known weight of the sample to be separated was thoroughly mixed with the mixture having the desired specific gravity. This mixture was then poured into a special glass vessel (see reference (1) p. 24) and allowed to sit undisturbed. When it had separated, the floating fraction was carefully removed. The separated fractions were then : filtered, washed with 100 ml of 1,1,1-trichloroethane, dried overnight in air and weighed.

#### (iv) Analysis

Proximate analysis (ash, volatiles and moisture) were carried out at Carleton University. Some ash and all sulfur determinations were performed at CANMET in Ottawa.

#### (v) Gas Adsorption

Samples of approximately 1 to 2 g were degassed under vacuum at 105 to 110 °C overnight (about 18 h). It has been reported that degassing for longer periods at temperatures of up to 150 °C does not significantly affect the surface areas obtained (26). Surface areas were determined from carbon dioxide adsorption at 298 K using the Polanyi-Dubinin isotherm (27). An arbitrary equilibration time of 30 min was allowed for each adsorption point. It has been reported that this is sufficiently long to obtain reliable surface areas (28).

## RESULTS

### (1) Acid Leaching Studies

#### (i) Proximate Analysis

Table I shows the proximate analysis of both lots of Balmer rejects received from CANMET.

#### (ii) Preliminary Studies

Lot 1 was ground and sieved to 0 x 18, 18 x 80, and 80 x 0 mesh size fractions. After some initial experiments and consultations with Dr. Nandi at CANMET, it was decided to study only the 18 x 80 and 80 x 0 mesh fractions. Initially two 50 g samples of each size consist were suspended in 250 ml of 10% (by volume) hydrochloric acid for 45 min at  $35 \pm 1^\circ\text{C}$ . One of each pair of samples was also exposed to ultrasonic irradiation for 30 min of the total HCl exposure time. The larger glass insonation cell (see experimental) was used for these experiments. These samples were all vacuum dried for a period of 24 h and subjected to a specific gravity separation at 1.64. The fraction (by weight) of the total material floating at 1.64 is given in table II.

Table I Proximate Analysis Of Balmer Rejects As Received  
From CANMET.

| LOT<br>NO. | ASH<br>% | VOLATILES<br>% | FIXED CARBON<br>% |
|------------|----------|----------------|-------------------|
| 1*         | 52.05    | 15.62          | 31.45             |
| 2          | 56.67    | 15.26          | 27.71             |

\* determined by CANMET.

Table II Fraction Of Total Material Floating At A Specific  
Gravity Of 1.64.

| SAMPLE<br>TREATMENT | SIZE<br>FRACTION | FLOATS AT<br>1.64<br>% |
|---------------------|------------------|------------------------|
| Untreated           | 80 x 0           | 57                     |
| HCl only            | 80 x 0           | 61                     |
| HCl + US            | 80 x 0           | 63                     |
| Untreated           | 18 x 80          | 40                     |
| HCl only            | 18 x 80          | 40                     |
| HCl + US            | 18 x 80          | 42                     |

In view of the small differences shown in table II, it was decided to focus on the 80 x 0 mesh fraction only. Two samples of this size fraction were exposed to 10% (by volume) HCl under conditions that were identical to those employed above with the following exceptions:

(1) only 20 g of sample was used (due to a shortage of coal supplied from CANMET) in 200 ml of HCl

(2) The smaller glass insonation cell (see experimental section) was used for sample treatment in order to achieve more effective exposure of the coal to the ultrasound,

(3) samples were washed with distilled water until no trace of chloride was detected (by a silver nitrate indicator) in the filtrate,

(4) Samples were air dried overnight (about 18 h) before they were subject to separations at specific gravities of 1.64 and 1.55.

These samples were analyzed for their ash contents, the results of this analysis are listed in table III.

Table III Ash Content Of 80 x 0 Mesh Fraction Separated At  
Specific Gravities Of 1.55 And 1.64.

| SAMPLE    | PERCENT<br>FLOAT |           | ASH CONTENT |           |           |           |           |
|-----------|------------------|-----------|-------------|-----------|-----------|-----------|-----------|
|           | 1.55<br>%        | 1.64<br>% | WHOLE<br>%  | FLOAT     |           | SINK      |           |
|           |                  |           |             | 1.55<br>% | 1.64<br>% | 1.55<br>% | 1.64<br>% |
| Untreated | 34               | 57        | 40.31       | 17.41     | 24.47     | 35.00     | 51.76     |
| HCl       | 33               | 61        | 40.12       | 17.55     | 27.14     | 38.93     | 62.56     |
| HCl + US  | 33               | 79        | 40.63       | 20.69     | 30.47     | 36.92     | 56.87     |

Table IV Proximate Analysis Of Some Representative Samples  
Of The 80 x 0 Mesh Fraction.

| SAMPLE<br>TREATMENT          | ASH   | VOLATILES | FIXED CARBON |
|------------------------------|-------|-----------|--------------|
|                              | %     | %         | %            |
| Untreated<br>(Whole)         | 40.31 | 17.51     | 41.74        |
| HCl + US<br>(Whole)          | 40.63 | 15.08     | 43.90        |
| HCl + US<br>(Floats at 1.64) | 30.47 | 15.75     | 53.78        |

It is clear from the results in tables II and III that the treatments employed have little effect on the ash content of the Balmer rejects. It is possible that a more prolonged treatment at higher temperatures would improve the results. The figures in table III also indicate that treatment reduces the efficiency of the separation step even though the overall ash content of the material is essentially unchanged by treatment. This is likely the result of the production of finer particles which interfere with specific gravity separations.

A full proximate analysis was only performed on three of these samples. Table IV shows the results of this analysis. The data in table IV indicate that treatment of the 80 x 0 mesh fraction with HCl and ultrasound results in an increase of about 2% in the fixed carbon content (which results from a 2% reduction in volatile materials). The reasons for such a change are not clear at this time. A simple specific gravity separation at 1.64 gives a floating fraction with a fixed carbon content which is about 10% higher than the unseparated material.

#### (iii) Effect of Particle Size

After discussions with Dr. Nandi at CANMET, it was

decided to use four narrower particle size fractions for the acid leaching studies. For this purpose, lot 2 of the Balmer rejects was ground and sieved to the following size consists: 18 x 35, 35 x 60, 60 x 120, and 120 x 0 mesh. Two 20 g samples of each size consist were treated with 200 ml of 10% (by volume) HCl for 90 min at  $70 \pm 1$  °C. One sample of each pair was also exposed to ultrasound (in the previously described smaller cell) for 80 min of this period. This material was subjected to a separation at a specific gravity of 1.65 and analyzed for its ash content. Tables V to VII show the results of these analysis.

The uniformity with which the mineral matter is dispersed throughout the Balmer rejects is demonstrated by the figures in table V. A particle size difference of a factor of eight between the largest and smallest size fractions results in a difference in ash contents of only 21%.

Table V Ash Content Of Untreated Balmer Rejects As A  
Function Of Size Fraction And Specific Gravity.

| SIZE<br>FRACTION | PERCENT<br>FLOAT<br>AT 1.65<br>% | ASH CONTENT |                    |                   |
|------------------|----------------------------------|-------------|--------------------|-------------------|
|                  |                                  | WHOLE<br>%  | FLOAT<br>1.65<br>% | SINK<br>1.65<br>% |
| 120 x 0          | 44.5                             | 44.27       | 22.37              | 62.56             |
| 60 x 120         | 35.3                             | 51.73       | 22.05              | 67.42             |
| 35 x 60          | 28.5                             | 57.14       | 23.89              | 69.88             |
| 18 x 35          | 23.2                             | 65.21       | 25.19              | 73.97             |

Table VI Ash Content Of Balmer Rejects Treated With  
HCl At 70 °C For 90 min As A Function Of Size  
Fraction And Specific Gravity.

| SIZE<br>FRACTION | PERCENT<br>FLOAT<br>AT 1.65<br>% | ASH CONTENT |                    |                   |
|------------------|----------------------------------|-------------|--------------------|-------------------|
|                  |                                  | WHOLE<br>%  | FLOAT<br>1.65<br>% | SINK<br>1.65<br>% |
| 120 x 0          | 50.4                             | 42.44       | 23.90              | 60.91             |
| 60 x 120         | 41.4                             | 50.15       | 21.27              | 70.10             |
| 35 x 60          | 31.3                             | 56.30       | 23.49              | 71.90             |
| 18 x 35          | 25.2                             | 62.72       | 24.89              | 77.31             |

Table VII Ash Content Of Balmer Rejects Treated With  
HCl At 70 °C For 90 min And Ultrasound For  
80 min As A Function Of Size Fraction And Specific  
Gravity.

| SIZE<br>FRACTION | PERCENT<br>FLOAT<br>AT 1.65<br>% | ASH CONTENT |                    |                   |
|------------------|----------------------------------|-------------|--------------------|-------------------|
|                  |                                  | PHOLE<br>%  | FLOAT<br>1.65<br>% | SINK<br>1.65<br>% |
| 120 x 0          | 40.7                             | 42.15       | 32.09              | 49.12             |
| 60 x 120         | 41.5                             | 48.73       | 32.55              | 61.23             |
| 35 x 60          | 17.1                             | 55.60       | 27.15              | 63.00             |
| 18 x 35          | 24.0                             | 63.83       | 29.82              | 77.76             |

As indicated in tables V-VII, all size fractions showed a slight reduction in their ash contents after treatment with HCl (about 1 to 2.5%). Treatment with ultrasound generally resulted in slightly greater ash reductions (about 1.4 to 3%) than treatment with HCl alone. This indicates that a small amount of the mineral matter was dissolved during treatment.

From the results of tables V-VII, it is clear that:

(1) a lower percentage of the total material floated at a specific gravity of 1.65 when it had been previously treated with ultrasound,

(2) samples treated with HCl alone showed a slight increase in the amount of floating material,

(3) there was little difference in the ash contents of the floating fractions of untreated samples and samples treated with HCl alone,

(4) In general, the sinking fraction of samples treated with HCl had slightly higher ash contents than did the sinking fractions of untreated samples,

(5) Treatment with ultrasound resulted in a substantial increase (about 4.6 to 10.5%) in the ash contents of the floating fraction. A similar decrease was observed in the ash contents of the sinking fraction for samples treated with ultrasound.

(6) A substantial increase in the amount of small sized particles was visible after treatment with ultrasound.

The fine particles noted above were likely formed by the intense mechanical shocks associated with cavitation. Additionally one would expect the vigorous agitation would cause some size reduction as particles collide with each other. Such fine particles would reduce the efficiency of a normal gravity separation. This would account for the poorer separation obtained after the samples were treated with ultrasound. The ultrasound could cause changes in the surface characteristics such as wetting and an expulsion of small gas bubbles could also be partly responsible for the changes in separation efficiency.

## (2) Ammonia Treatment

### (i) Introduction

The use of chemicals such as ammonia for comminution of coal has been the subject of several reports (29-35). It has been reported that treating coals with liquid ammonia and other non-aqueous liquids causes selective cracking along the boundaries between mineral matter and the organic coal matrix (30-33). One study has reported no such selectivity when high

sulfur Prince coal was treated with liquid ammonia (35). After consulting with Dr. Nandi at CANMET it was decided to treat Prince coal and Balmer rejects with ammonia in the presence of ultrasound. A concentrated solution of ammonia (about 20% by weight) in methanol was used so that neither high pressure nor low temperature conditions were required for the treatment. Methanol was selected for the solvent because ammonia is extremely soluble in it and because methanol is also reported to be a good comminuting agent (30).

#### (ii) Prince Coal

Samples of Prince coal (20 g) were treated in 200 ml of ammonia solution at  $6 \pm 2$  °C. Samples were then rinsed with methanol and dried. The treated samples were analyzed for their sulfur and ash content after being separated at a specific gravity of 1.30. Table VIII shows the results of these analysis for the 20 x 0 mesh Prince coal

The results in table VIII show an increase in the amount of floats, at a specific gravity of 1.30, after all treatments of the 20 x 0 Price coal. The greatest increase was obtained when the coal was exposed to a 20% ammonia/methanol solution for 120 min without

Table VIII Effect Of Treatment On The Ash And Sulfur Content  
Of 20 x 0 Prince Coal.

| TREATMENT                              | PERCENT FLOAT<br>AT 1.30<br>% | ASH         |            | SULFUR      |            |
|----------------------------------------|-------------------------------|-------------|------------|-------------|------------|
|                                        |                               | FLOATS<br>% | SINKS<br>% | FLOATS<br>% | SINKS<br>% |
| Untreated*                             | 30.8                          | 2.01        | 35.13      | 1.59        | 4.49       |
| Methanol +<br>Ammonia<br>(120 min)     | 41.9                          | 1.51        | 39.60      | 1.71        | 4.95       |
| Methanol +<br>Ammonia<br>(70 min)      | 38.1                          | 2.03        | 38.16      | 1.71        | 4.75       |
| Methanol +<br>Ammonia + US<br>(70 min) | 35.5                          | 1.67        | 35.87      | 1.62        | 4.35       |
| Methanol<br>(70 min)                   | 36.2                          | 2.05        | 35.71      | 1.66        | 4.64       |

\* Whole sample contains 24.58% ash, 3.79% sulfur and 10.61% oxygen.

Ammonia concentration =  $20 \pm 2\%$  by weight.

Figures in brackets indicate length of contact time.  
Ultrasound was applied for the full contact period.

ultrasound. A reduction of the exposure time to 70 min resulted in a 3.8% reduction in the amount of floating material. A further reduction of 1.9% occurred when only methanol was used. Treatment with intense ultrasound during a 70 min exposure to an ammonia/methanol solution caused an additional 0.7% reduction in the amount of floating material. It is likely that the overall increase in the amount of floats results from swelling effects. It is well known that both ammonia and methanol are imbibed by coals causing them to swell (29).

The lowest ash contents are obtained in the floating fractions of samples that had been treated with ammonia/methanol solutions for 120 min without ultrasound and for 70 min with ultrasound. However, it is difficult to say if the difference in the ash contents of these samples and those of the others is significant.

There is very little change in the sulfur content with any of the treatments. It is possible that much of the remaining sulfur is organic sulfur which would require more vigorous chemical methods to remove. In reference (35) Prince coal is reported to have an organic sulfur content of about 1.20%. This would constitute the major part of the residual

sulfur in the floating material.

All samples were different in their appearance after treatment with ammonia/methanol solutions. The particles in these samples were noticeably darker and shinier than were those in the original material. It is likely that this treatment chemically modifies the coal surface. It has been reported that ammonia reacts with oxygen containing functionalities in the coal surface such as phenol groups (36). This results in the formation of nitrogen containing groups such as amides and an increase in the gasification reactivity (37). Such a chemical change might be expected to produce a change in the physical appearance of the coal.

The 100 x 0 mesh Prince coal was also treated as described above. An attempt to achieve a separation at a specific gravity of 1.30 gave a minuscule floating fraction (<3%). Analysis of the whole samples for their ash and sulfur contents yielded the values given in table IX.

Treatment of the 100 x 0 mesh Prince coal had little effect on its overall ash or sulfur content. This material did not float at a specific gravity of 1.30. It is possible

that pores within the coal, which were not accessible to the separation liquid in the coarser material, are made accessible after grinding to this small size. This would result in an increase in the effective density of the coal. This hypothesis is supported by the observation that the floating fraction of the 20 x 0 mesh Prince coal was much coarser than the sinking fraction. This may also explain the decrease in the amount of floating material when ultrasound was applied to the 20 x 0 mesh fraction in ammonia/methanol solutions. It is likely that ultrasonic treatment would cause some comminution.

#### (iii) Balmer Rejects

Samples of 35 x 60 mesh Balmer rejects were treated in a similar manner to the Prince coal. On the advice of authorities at CANMET, these samples were treated in methanol for 24 h at room temperature before further treatment. These samples were separated at a specific gravity of 1.65 and analyzed for their ash contents. The results of this analysis are given in table X. These samples also showed a change in appearance which was similar to, but not as pronounced as, that observed with the Prince coal.

Table IX Effect Of Treatment On The Ash And Sulfur Content  
Of 100 x 0 Prince Coal.

| TREATMENT                              | ASH<br>% | SULFUR<br>% |
|----------------------------------------|----------|-------------|
| Untreated*                             | 24.57    | 3.68        |
| Methanol +<br>Ammonia<br>(70 min)      | 23.22    | 3.32        |
| Methanol +<br>Ammonia + US<br>(70 min) | 24.55    | 3.69        |

\* Whole sample contains 10.31% oxygen.

Ammonia concentration =  $20 \pm 2\%$  by weight.

Figures in brackets indicate length of contact time.  
Ultrasound was applied for the full contact period.

The data in table X indicate that treatment with ammonia/methanol solutions has little effect on the ash content of Balmer rejects. The application of intense ultrasound during this treatment also had little effect. It is likely that a chemical change of the coal surface, similar to that suggested for the Prince coal, occurred during the treatment. This may have some beneficial effects on the gasification reactivity of Balmer rejects.

### (3) Treatment In Aqueous Suspension

#### (i) Balmer Rejects

Two samples of Balmer rejects (35 x 60 and 60 x 120 mesh) were treated with ultrasound in 200 ml of water at  $70 \pm 1$  °C. The 60 x 120 mesh sample was separated at 1.65 and analyzed for its ash content. The 35 x 60 mesh sample showed a particle size reduction which was similar to that noted when samples were treated with ultrasound in HCl. After treatment 33.1% of the total sample was able to pass through a 60 mesh screen whereas none of the original material was able to do so. These samples were also much easier to grind than were those treated in other ways. Table XI shows the ash contents of the treated samples.

Table X Effect Of Treatment On The Ash Content  
Of 35 x 60 Balmer Rejects.

| TREATMENT                              | PERCENT FLOATS<br>AT 1.65<br>% | ASH         |            |
|----------------------------------------|--------------------------------|-------------|------------|
|                                        |                                | FLOATS<br>% | SINKS<br>% |
| Untreated                              | 28.5                           | 23.89       | 69.88      |
| Methanol +<br>Ammonia<br>(180 min)     | 30.4                           | 23.22       | 70.62      |
| Methanol +<br>Ammonia + US<br>(70 min) | 23.7                           | 22.93       | 68.09      |

Ammonia concentration =  $20 \pm 2\%$  by weight.

Figures in brackets indicate length of contact time.  
Ultrasound was applied for the full contact period.

The treatment of Balmer rejects with ultrasound resulted in a slight reduction of their ash content. Comparing the results in tables V and XI, it can be seen that treatment for 30 min with ultrasound caused a 0.5% reduction in the ash content of the 60 x 120 mesh sample. A reduction of 1.91% was obtained by treating the 35 x 60 mesh sample for 80 min.

The most striking effect of treatment with ultrasound in water was the degree of comminution that occurred. This was probably caused by the same mechanism postulated for the samples treated with HCl and ultrasound.

It is possible that the increased friability of the material after treatment in water was resulted from swelling of clay material trapped in fissures and pores within the coal matrix. Intense ultrasound might improve the clay-water contact by streaming and "micro-pumping". It is possible that cracks and pores are caused to open and close by cavitation and cyclic pressure fluctuations due to the ultrasound. This would cause a "micro-pumping" of water into and out of the coal cracks in the coal material and expose clay trapped deeply within these cracks to water. The swollen clay might cause some fracturing of the coal and perhaps the non-clay minerals. This would facilitate grinding of this material.

(ii) Prince Coal

All samples of Balmer coal which had been treated with ultrasound in aqueous suspension showed some signs of comminution. Thus, a sample of 20 x 0 mesh Prince coal was treated with an ammonia/methanol solution in the absence of ultrasound for 120 min. the sample was then dried and exposed to ultrasound in water at  $70 \pm 1$  °C for 30 min. It was hoped that the ammonia treatment would cause some cracking along the boundaries between the mineral matter (pyrites) and the organic coal matter. The subsequent exposure to ultrasound in water might therefore dislodge the inorganic matter from the coal. The sample treated in this manner was separated at a specific gravity of 1.30 and analyzed for its sulfur and ash content. Table XII shows the results of this analysis.

The results in table XII show that the major effect of treating the 20 x 0 mesh Prince coal in water with ultrasound (after it had been initially exposed to an ammonia/methanol solution) is a reduction in the amount of floating material. The treated material had undergone a significant degree of comminution during treatment. It is likely that the finer particles so produced would not float for the same reasons

Table XI Ash Content Of Balmer Rejects Treated With  
Ultrasound In Aqueous Suspension.

| SIZE<br>FRACTION        | PERCENT<br>FLOAT<br>AT 1.65<br>% | ASH CONTENT |             |            |
|-------------------------|----------------------------------|-------------|-------------|------------|
|                         |                                  | WHOLE<br>%  | FLOATS<br>% | SINKS<br>% |
| 60 x 120*               | 33.6                             | 51.24       | 31.47       | 61.41      |
| 60 x 0                  | -                                | 51.73       | -           | -          |
| 35 x 60                 | -                                | 63.61       | -           | -          |
| 35 x 60<br>(originally) | -                                | 55.23       | -           | -          |

\* Exposed to ultrasound for 80 min out of 90 min total treatment time.

Exposed to ultrasound for total treatment time of 120 min.

Material originally 35 x 60 mesh, separated into 35 x 60 and 60 x 0 mesh fractions.

Table XII Effect Of Treatment In Aqueous Suspension On The  
Ash And Sulfur Content Of 20 x 0 Prince Coal.

| TREATMENT                              | PERCENT FLOAT<br>AT 1.30<br>% | ASH         |            | SULFUR      |            |
|----------------------------------------|-------------------------------|-------------|------------|-------------|------------|
|                                        |                               | FLOATS<br>% | SINKS<br>% | FLOATS<br>% | SINKS<br>% |
| Untreated*                             | 30.8                          | 2.01        | 35.13      | 1.59        | 4.49       |
| (1) Methanol +<br>Ammonia<br>(120 min) | 7.4                           | -           | 23.78      | 1.57        | 3.00       |
| (2) Water + US<br>(30 min)             |                               |             |            |             |            |

\* Whole sample contains 24.58% ash, 3.79% sulfur and 10.61% oxygen.

Ammonia concentration =  $20 \pm 2\%$  by weight.

Figures in brackets indicate length of contact time.  
Ultrasound was applied for the full contact period.

that the 100 x 0 mesh samples would not float.

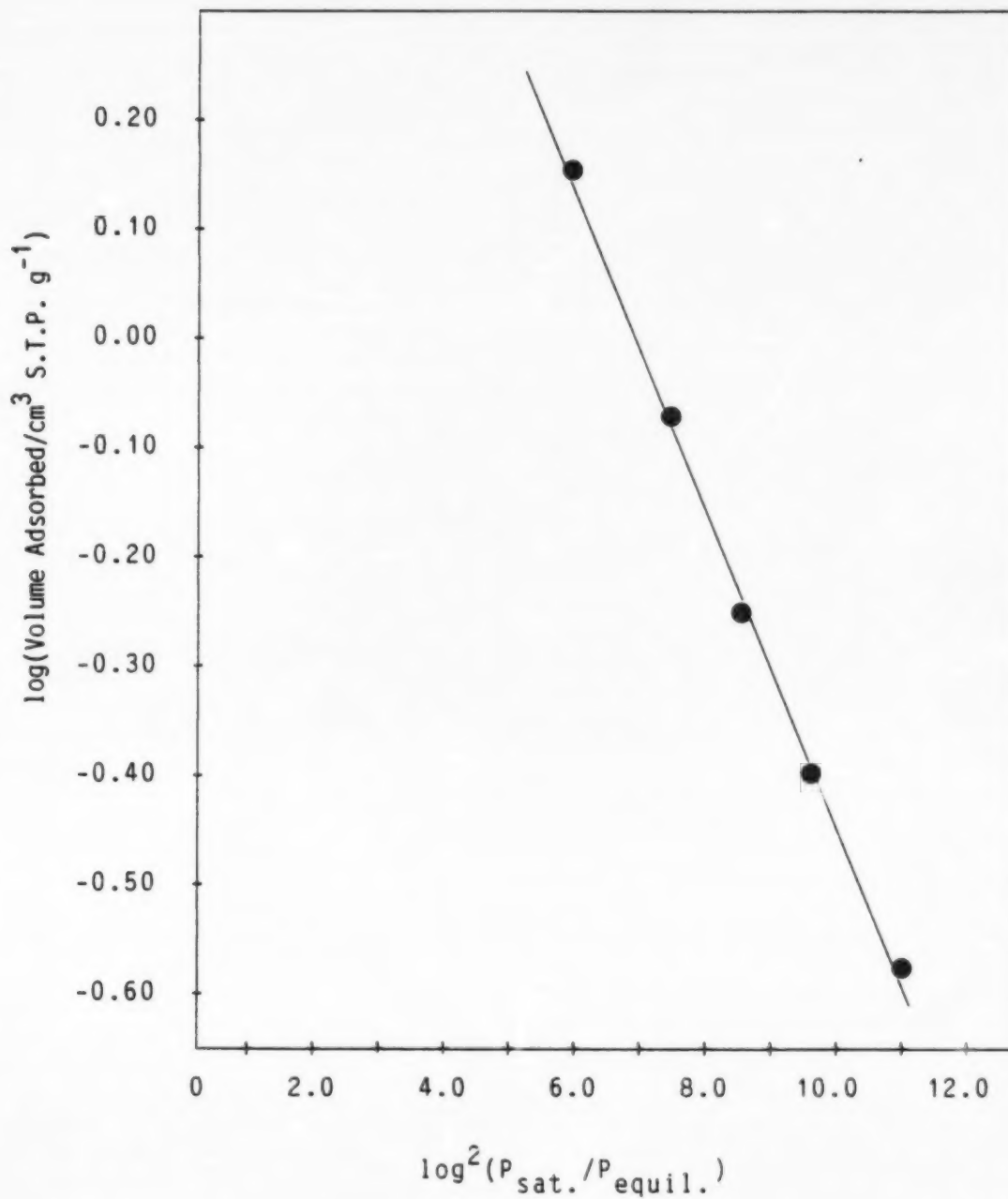
#### (4) Gas Adsorption

It has been reported that the porosity and surface area of a given coal can strongly affect its gasification reactivity (38,39). Thus, the surface areas of samples of treated and untreated Balmer rejects were determined by the adsorption of carbon dioxide at 298 K using the Polanyi-Dubinin isotherm. Samples of untreated 35 x 60 mesh Balmer rejects and 35 x 60 mesh Balmer rejects which had been treated with ultrasound in aqueous suspension at  $70 \pm 1$  °C for 120 min were used for this purpose. The treated sample showed a significant degree of comminution (see section 3 (i) above). Consequently, it was resieved and only the 35 x 60 mesh material used for the surface area measurement.

Two samples (about 5 g each) of 50 x 0 mesh Balmer coal were obtained from Dr. Nandi at CANMET. One of these samples was fresh coal while the other had been oxidized at 35 °C for one week. The surface areas of these samples were also determined as has been described above.

A sample Polanyi-Dubinin plot is shown in figure 1.

Figure 1 Polanyi-Dubinin Isotherm For The Adsorption  
Of Carbon Dioxide On Untreated 35 x 60  
Mesh Balmer Coal Rejects At 298 K.



Excellent linearity was obtained in this and all other plots. Correlation coefficients of better than 0.999 were obtained in all cases. The surface areas were obtained from the intercepts of such plots using values of  $0.253 \text{ nm}^2$  (28) and 43,800 torr (27) for the molecular area and saturation vapor pressure of carbon dioxide at 298 K respectively. Table XIII shows the values of the surface areas obtained for these samples.

When one considers the drastic comminution effect observed after treatment of Balmer rejects with ultrasound in water, one might expect a significant change in the surface area. The results in table XIII show that Balmer rejects have a slightly (but significantly) smaller surface area after treatment. This difference disappears completely after the results are corrected for the ash content of the samples (see table XI).

The surface areas of both treated and untreated Balmer rejects are still much lower than that of fresh Balmer coal, even after correction for ash content. It has been suggested (40) that the Balmer rejects are very highly oxidized. It has also been reported that oxidation reduces the surface area of coals by blocking some of the pores (38).

Table XIII Effect Of Treatment On The Specific Surface

Areas Of Balmer Coal And Balmer Coal Rejects.

| SAMPLE                      | TREATMENT  | SPECIFIC SURFACE AREA     |                           |
|-----------------------------|------------|---------------------------|---------------------------|
|                             |            | AS DETERMINED             | DRY ASH FREE              |
|                             |            | $\text{m}^2\text{g}^{-1}$ | $\text{m}^2\text{g}^{-1}$ |
| Balmer<br>Rejects           | untreated  | 64±3                      | 151±7                     |
| Balmer<br>Rejects           | water + US | 54±3                      | 150±8                     |
| Balmer <sup>*</sup><br>Coal | Fresh      | 155±6                     | 170±6                     |
| Balmer<br>Coal              | oxidized   | 162±5                     | 178±8                     |

\* Ash content 9%.

Thus, it might be expected that oxidation could account for the observed differences. From table XIII it is evident that oxidation of Balmer coal has negligible effect on its surface area. Consequently, the difference might be explained by the following:

(1) a blockage of some pores by mineral matter in the rejects leading to a lower surface area,

(2) a difference in the maceral composition (it is known that the surface area is also affected by the proportion of different macerals within the coal (38)),

(3) a difference in the size consist. The Balmer coal samples were 50 x 0 mesh while the rejects were 35 x 60 mesh. Unfortunately Balmer coal of the same size consist was not obtainable.

### CONCLUSIONS

The application of intense ultrasound to the processing of Balmer coal rejects and Prince coal has been investigated. Experimental results show that intense ultrasound causes a slight acceleration in the rate of leaching Balmer rejects with dilute hydrochloric acid. This can be attributed to increased agitation and more intimate mixing of the reactants. A small reduction (about 2%) in the volatile content of Balmer

rejects occurred when they were treated with ultrasound in dilute HCl. The reasons for this are not clear at this time. A slight (0.5 to 1.9%) reduction in the ash content of Balmer rejects occurred when they were treated in water with intense ultrasound. Treatment with ultrasound in both water and dilute HCl caused a considerable comminution of both Balmer rejects and Prince coal. This may be attributed to cavitation shock waves, violent agitation and swelling of trapped clay material.

Treating Prince coal and Balmer rejects with solutions of ammonia (20% by weight) in methanol had little effect on their ash or sulfur contents. The application of ultrasound during this treatment was also ineffective. However, a significant change in the appearance of both coals occurred after treatment which may indicate a chemical change of their surfaces. This may have beneficial effects on the gasification reactivity of these coals. Further study is required to determine what the cause of these changes and their possible effect on the reactivity of these coals.

The specific gravity separations employed in this work are not effective. The treatments applied to the coals in this work generally resulted in poorer separations. Some

of this problem can be traced to the comminution produced by the treatments. Cavitation occurs at the surfaces of particles suspended in liquids. The large forces which arise from this phenomenon can clean the particles of surface films. Thus, an alternate separation method such as froth flotation would probably be more compatible with the treatment effects.

The surface area (daf) of the Balmer rejects was not significantly changed by treatment with ultrasound in water. Thus, a significant change in the gasification reactivity of this material would not be expected. However, larger and more regular coal supplies would be needed to undertake a definitive study.

### RECOMMENDATIONS

The results of the present work have shown a slight improvement in the rate of Balmer reject demineralization, by leaching with dilute hydrochloric acid when intense ultrasound is applied. Substantial acceleration and enhancement of chemical leaching processes have been associated with the application of intense ultrasound (12,15,16). More work is required to find a combination of leachants and conditions which would prove more effective in treating Balmer rejects than those employed in this work. Such work could also be extended to the desulfurization of high sulfur coal since most of the success reported in the literature has been in this direction.

High levels of sodium in many lignites can cause severe boiler fouling. It may be possible to reduce this problem by removal of the sodium through an ion exchange process. Intense ultrasound would likely accelerate this process and may even increase the extent to which sodium is removed.

A more effective method for the physical separation of the coal from the mineral matter, after treatment, must be found. Unless some method can be found to reduce the comminution which occurs during treatment, a simple specific

gravity separation cannot be used effectively. Intense ultrasound may be very effective in cleaning the surface of coal particles thereby freeing them from surface films and trapped gas. The efficacy of separations such as froth flotation (2-4,8-11) and oil agglomeration (5-7) has been enhanced by applying intense ultrasound. Such separation methods may prove to be more effective.

The effects of treatments on the physical properties and reactivities of coal would be very useful. Properties such as: surface area, porosity, caking characteristics and others are known to drastically affect coal reactivity (37-39) but the effects of coal treatments on these properties has not been widely reported in the literature. It seems useful to carry out a study that would provide a greater fundamental understanding of the relationships between coal reactivity and the physical properties of coals, and the effect of treatments on the physical properties of coals.

This would lead to the design of more effective (and economical) treatments for coal processing. A thorough study of the type described above would require more time and a larger amount of coal (at least 10 to 20 kg) than available during this work.

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